

***Supplemental Comments* on the National Marine Fisheries Service
Draft Biological Opinion: “Environmental Protection Agency
Registration of Pesticides Containing Chlorpyrifos, Diazinon and
Malathion (July 31, 2008)**

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THE ENVIRONMENTAL FATE PROFILE FOR MALATHION AND DISCUSSION OF THE POTENTIAL FORMATION OF MALAOXON IN THE ENVIRONMENT

The NMFS BiOp raises concerns about the formation of malaoxon in the environment following malathion applications. This document reviews the results of the environmental fate studies, conducted according to EPA's environmental fate test guidelines, that have been submitted to EPA to support the registration of malathion. We then discuss the potential for malaoxon to form in the environment as a result of the application of malathion emulsifiable concentrate (EC), ultra low volume (ULV), and ready-to-use (RTU) formulations. Finally, we compare the results from the guideline environmental fate database on malathion, to the results obtained from the California EPA study on the environmental fate of malathion in a proteinaceous bait formulation historically used in fruit fly eradication and suppression programs in California.

I. OVERVIEW OF THE ENVIRONMENTAL BEHAVIOR OF MALATHION BASED ON THE SUBMITTED GUIDELINE ENVIRONMENTAL FATE STUDIES

The 1988 Registration Standard (EPA, 1988) required registrants to submit a full battery of environmental fate studies on malathion to support the continued registration of this compound in the United States. The submitted studies are listed in the bibliography at the end of this document. These studies include both laboratory and field experiments. The laboratory studies were conducted with technical malathion, or with C14-malathion. The field studies were conducted using typical malathion end-use formulations, such as the emulsifiable concentrate (EC), ultra low-volume (ULV), or ready-to-use (RTU) formulations. All studies were conducted, as required, according to EPA-approved testing methods and in accordance with Good Laboratory Practices (40 CFR Part 160). A brief overview of the results of this testing is provided below.

A. Overview of Laboratory Degradation Studies

In the guideline hydrolysis study (MRID 40941201), malathion was stable to hydrolysis at pH 5, but hydrolyzed at pH 9, with a calculated half-life of 12 hours, as is expected from

phosphorodithioate esters. Initial hydrolysis products (malathion mono-carboxylic acid (MCA), malathion di-carboxylic acid (DCA), desmethyl malathion, ethyl fumerate, and diethylthiosuccinate) did not degrade appreciably under the sterile conditions of this study. Malathion did not undergo photolysis upon exposure to artificial sunlight in air (MRID 40969301), aqueous solution (MRID 41673001), or on the surface of soil (MRIDs 41039001, 41695501, and 42015201). This lack of photolytic activity is expected, because the longest wavelength peak in the UV absorption spectrum of malathion is a shoulder of about 215 nm. Malathion has no absorption above about 260 nm; this onset of absorption is well below the lower limit of natural sunlight irradiation.

B. Overview of Laboratory Adsorption, Desorption and Mobility Studies

In a study reported in 1989 (MRID 41345201), the adsorption/desorption of malathion was studied in five soils with quite low levels of organic carbon: sandy loam from California, sand from Florida, loam from Missouri, silt-loam from Missouri, and sandy loam from Arkansas. Calculated adsorption K_{oc} -values varied from 151 to 308 ml/g, indicating that malathion is moderately mobile in soil.

The mobility of malathion and its metabolites was also assessed in four different soil types in an aged leaching study (MRID 43868601). After ageing 0.5-14 hours the soils contained approximately 38 – 60 % malathion, 7 – 20 % DCA and 16 – 34 % MCA. Following the leaching process, 48 – 74 % AR was found in the leachate in three of the soils but in the final soil (silty clay) only 5 % was found. The radioactivity in the three leachates consisted primarily of DCA (18 – 69 %) with smaller amounts of MCA (5 – 14 %). Parent malathion was only found in the leachate from the sandy soil, and at trace amounts (1.9 %). Malaoxon was not detected in this study.

C. Overview of Laboratory Metabolism Studies

In the 1990 aerobic soil metabolism study (MRID 41721701), a solution of ¹⁴C-malathion (purity 95.6%) and unlabelled malathion (purity 98.4%) in methanol was added to soil samples at a concentration of 6.88 mg/kg malathion. Malathion degraded rapidly in loam soil under aerobic conditions, with an estimated half-life of 0.2 days. The major degradate was DCA; it formed rapidly; however, it also decayed rapidly, as did all the other degradates. Malaoxon was found on samples collected immediately after application (day 0) at a maximum of 1% of applied radioactivity. However, according to the study contractors, the presence of malaoxon was assumed to be a contaminant in the radio-labeled test material. After seven days only 0.4% of the original radioactive dose was present as malathion, and all degradates had further degraded to less than 0.1% of the initial dose. The mineralization of malathion to ¹⁴C carbon dioxide reached 30% after three days and was approximately 50% after 90 days. Bound residues formed rapidly, reaching 60% in one day, and declined slowly, with continued release of ¹⁴C carbon dioxide. The fulvic acid and humin fractions of the soil contained the majority of the bound residues. Volatilization was not significant.

Similar results were seen in a second aerobic soil metabolism study conducted in 2001 (46769501). In this study, ¹⁴C-malathion was applied to four soils; Bergen-Enkheim silty clay, Hofheim silty loam, Lufa 2.1 sand, and Schwalback silty loam. Malathion was rapidly degraded in all four soils tested (half lives range from 0.17 to .25 days) to form MCA and DCA as the major degradates. Both of these degradates reached maximum levels of 25% at 8 hours post-application and 61.7% on day 1 and dissipated rapidly thereafter (half-lives for MCA were 0.12 to 0.65 days, and half-lives for DCA were 1.2 to 5.3 days). The ultimate fate of malathion was the formation of CO₂, with smaller amounts of bound residues formed. Malaoxon was never detected in this study.

In an anaerobic aquatic metabolism study (42216301), malathion degraded in a sandy loam soil/water mixture under anaerobic conditions, with a half-life of 2.5 days. After 14 days into the study, no malathion was detectable. The major degradates MCA, DCA and two corresponding to des-methyl mono and diacids formed rapidly and were found predominantly in

the water phase. MCA and DCA were completely metabolized by day 62, and all metabolites were completely degraded by 118 days. The mineralization of malathion to ¹⁴C carbon dioxide reached 55% after 118 days.

C. Summary of Field Dissipation Studies

Field dissipation studies carried out in California and Georgia on cotton (MRIDs 41727701, 41748901, 43043401, and 43042402) and bareground soil plots showed that malathion dissipated very rapidly after a series of six sequential applications. In the California study, residues of malathion averaged 0.097 ppm in 0-6 inch cores immediately after application; no residues were detectable after 14 days in these cores. No malathion was detected in lower core segments, except that one of three composite samples at the 18-24 inch depth had 0.068 ppm seven days after the last application. In the bareground plot, only a single composite sample had detectable residues at the 6-12 inch depth. The analytical results from the cotton and bareground plots in the Georgia study were very similar. Taken together, these field results demonstrate that malathion dissipates rapidly and does not move downward under normal California or Georgia field conditions.

It is important to note that no malaoxon was detected in either the California or Georgia field soil dissipation studies. In additional research carried out on these studies, soil samples from all test plots in each study were analyzed for DCA, which is the initial major metabolite found in the aerobic aquatic metabolism study. In the California field dissipation study, residue levels of DCA averaged 0.055 ppm in the 0-6 inch soil layers in both bareground and cropped plots immediately after applications; these residues also dissipated rapidly, with half-lives of about three days. In the bareground plot, no DCA residues were detected in the 6-12 inch soil layer at any time; in the cropped plot, levels of DCA averaged about 0.04 ppm immediately after application and also dissipated, with a half-life of about 3 days. No DCA residues were detected in the 12-18 inch layer at any time. Analysis of soil samples from the Georgia site detected similar levels of DCA residues immediately after application; dissipation of these residues was too rapid to estimate a half-life.

An aquatic field dissipation study carried out in Missouri (MRID 42058402) also showed very rapid dissipation of malathion. Average residues of malathion after each of three applications to rice paddies were 0.64 ppm, 0.35 ppm, and 0.16 ppm. Residues levels averaged 0.016 ppm one day after the last application and were below the limit of detection of 0.01 ppm in all subsequent samples.

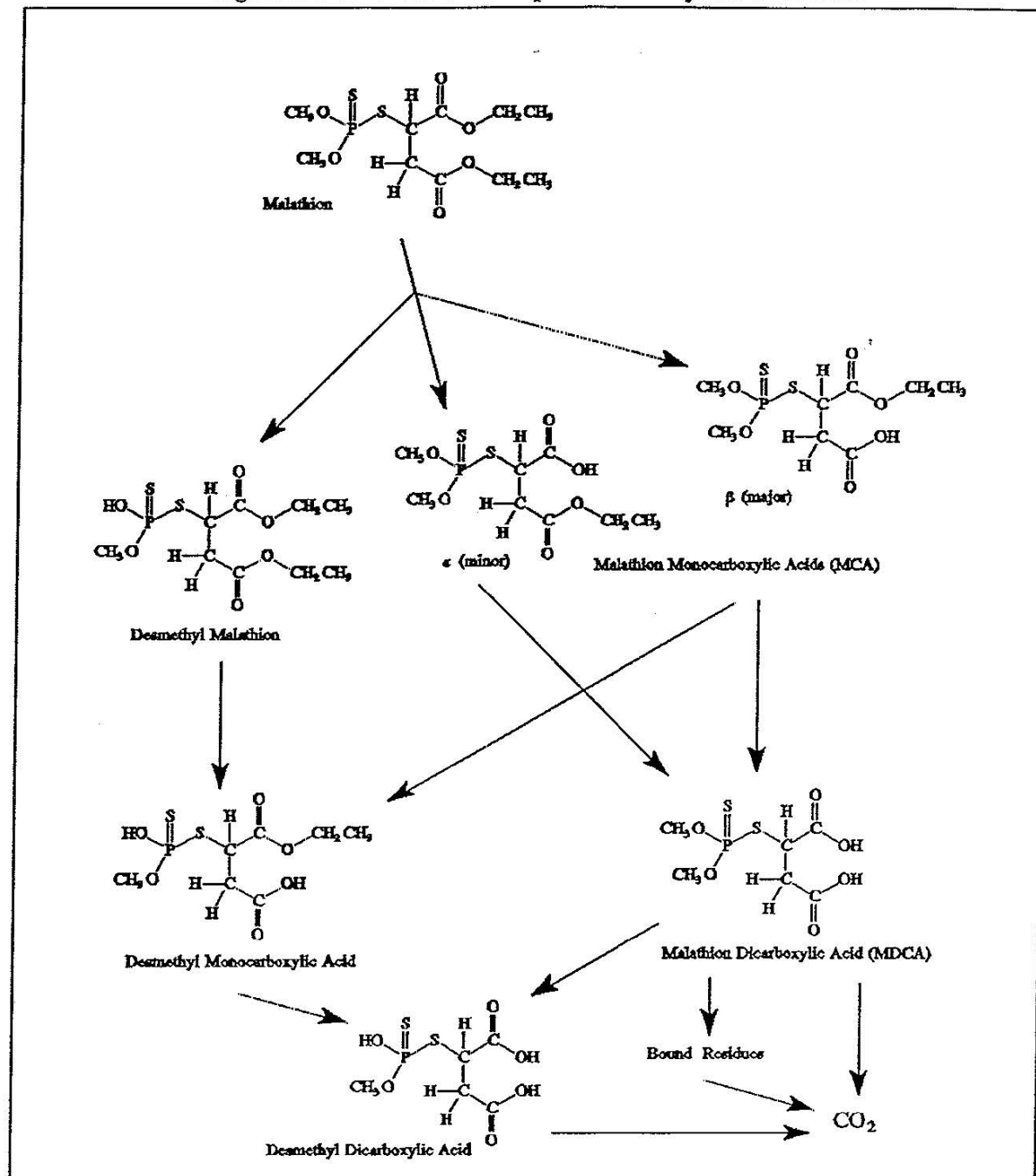
Similar results were seen in a separate aquatic dissipation study conducted in California (MRID 42058401). In this study, the ULV formulation of malathion was applied at a rate of 0.58 lbs ai/A in three weekly applications to flooded plots. The initial concentrations of malathion in water were about 0.02 ppm in this study. Malathion concentrations degraded rapidly with an apparently half-life of < 1 day. No malaoxon was detected in this study.

D. Summary of the Environmental Fate of Malathion

These environmental fate studies provide a consistent picture of rapid degradation of malathion in the environment after application. The pathway of environmental dissipation is shown in Figure 1. Dissipation is dominated by microbially mediated processes. The initial step is de-esterification to form the less toxic MCA and DCA; demethylation of phosphorus ester groups also occurs rapidly. These metabolites are further degraded in soil, ultimately leading to complete degradation of the malathion molecule and production of carbon dioxide. Overall half-lives under both laboratory and field conditions are about one to two days for degradation of parent malathion and only slightly longer for disappearance of the initial carboxylic acid metabolites. Similarly, malathion rapidly degraded in a water/sediment mixture (half-life of 2.5 days). The rapid degradation of malathion in surface soil means that downward movement of malathion residues will not be significant, even under conditions favorable to leaching. The studies also demonstrated the ultimate mineralization of malathion into CO₂.

The next section will turn to specific results for malaoxon detection in the available fate studies.

Figure I. Environmental Dissipation Pathways for Malathion



II. THE POTENTIAL FORMATION OF MALAOXON

A. Studies Related to Agricultural Uses

Of all the guideline studies submitted to support the registration of malathion, only one laboratory study (an aerobic soil metabolism study, MRID 41721701) identified measureable residues of malaoxon after application of malathion. In guideline field studies, no malaoxon was detected in two soil dissipation studies or in two aquatic dissipation studies.

The aerobic soil metabolism study (MRID 41721701) was a laboratory test conducted using radiolabeled malathion applied to a soil that is typical of agricultural soils in Missouri. The levels of malaoxon formed after the application in this study are summarized in Table 1 (average of two duplicate samples at each time point are shown). A very small amount of malaoxon was present immediately after the application at <1% of the applied malathion. However, by 24 hours, the level was reduced to 0.2%, by 3 days it was 0.1%, and by day 7 it was not detectable. Since malaoxon was seen in the soil sample collected immediately after application (on day 0), it is likely that malaoxon was probably introduced as a contaminant in the radiolabelled material applied to the soil.

Table 1. Malaoxon levels in the U.S. aerobic soil metabolism study

Time After Application	Malaoxon Level (% of applied)
0	0.95%
6 hours	0.8%
1 day	0.2%
2 days	0.25%
3 days	0.1%
4 days	0.1%
7 days	Nd
14 days	Nd
92 days	Nd

Nd: not detected

Additionally, four aerobic soil metabolism measurements were made in a European Union study (MRID 46769501). The study included a two silty loam soils, silty clay, and a sand soil. Malaoxon was not detected in any of the soils at any time period. Another EU study (MRID 46769502) evaluated the degradation of malathion in two water/sediment systems; malaoxon was not detected in either system at any time period. The results of these two more recent studies in which malaoxon did not form, call into question the results obtained in the earlier aerobic soil metabolism study.

The result of the earlier aerobic soil metabolism study is further questioned based on the results of two guideline field soil dissipation studies discussed earlier that were conducted in Georgia (MRID 41748901) and California (MRID 41727701). In these studies, malathion was applied in the field and residues in soil were measured at different times after the application. Both studies were conducted on cotton and included an application on bare ground as a control plot. The studies included six weekly applications of the ULV formulation at 1.16 lbs per acre. There were no residues of malaoxon detected on either plot at any time after the application in either study.

Cheminova also submitted results from two aquatic field dissipation studies; one was conducted in Missouri (MRIDs 42058402 and 43166301) and the other was conducted in California (MRIDs 42058401 and 43166301). In both studies, the ULV formulation of malathion was applied at maximum rate of 0.58 lbs ai/A in three weekly applications to a flooded rice paddy. Malathion residues in the rice paddy averaged 0.38 ppm on the day of application. No malaoxon was detected in soil or water samples from either study (analytical limit of detection was 0.01 ppm).

The results of the aquatic field dissipation studies are consistent with the results seen in the laboratory in the guideline aerobic aquatic metabolism study (MRID 422716-01) – malaoxon was not detected in the aquatic environment.

B. Additional Comments about the Study by California EPA of a Malathion-Bait Formulation Used for Fruit Fly Eradication Programs.

As noted in our previous comments, there is one study conducted by California EPA (Cal EPA, 1993) in a laboratory greenhouse that was intended to investigate malaoxon formation following the simulated application of malathion in a protein bait. This bait formulation has historically been used as part of fruit fly (including the Mediterranean Fruit Fly) eradication efforts in California and in Florida. The limitations of the California EPA study were extensively discussed in our previous response to the draft BiOp. Cheminova does not consider those data to be relevant to malathion uses for the following reasons:

- Malathion was mixed with a proteinaceous bait. This bait mixture has been used in California only used for fruit fly eradication efforts. The bait mixture is not relevant to other agricultural, residential, or public health uses of malathion, and the historical use of the bait formulation as a wide-area treatment over urban areas is not supported by Cheminova.
- In the California EPA study, the malathion/bait mixture was spread on the test matrices as a thick slurry. This method of application is not at all representative of how the material would be applied in the field.
- California EPA stated that it believes the protein bait changed the environmental fate profile for malathion. Indeed, the California EPA theory is supported by a comparison of the extensive guideline environmental fate database for malathion (described above) with the unusual results seen in the California EPA study. In the guideline studies conducted with technical malathion and typical end-use formulations of malathion, a very minor amount of malaoxon was detected in only one of three aerobic soil metabolism studies; as discussed above, there are multiple reasons for questioning the validity of this finding., including the fact that no malaoxon was formed in any of the four guideline field dissipation studies. The different results seen in the California EPA study indicate that the bait, or the way the bait mixture was applied (as a slurry), likely changed the way malathion behaved in the environment.

Because this bait mixture is not used for anything other than these specific programs, there are significant questions about the relevancy of these data for consideration in the BiOp. The data clearly are not relevant for agricultural uses, where this formulation isn't used.

III. DISCUSSION AND CONCLUSION

In the guideline laboratory studies conducted with malathion, malaoxon has been detected in only one of several aerobic soil metabolism studies. In this single study, malaoxon was detected immediately after application at a very low level, and it quickly dissipated. The study contractor concluded that the presence of malaoxon on day 0 in this study was likely the result of malaoxon as a contaminant in the radiolabelled solution applied to the soil, rather than a metabolite or degradate. The presence of malaoxon was not confirmed in subsequent aerobic soil metabolism tests, nor in studies of hydrolysis and photolysis, leaching/adsorption/desorption, three subsequent aerobic aquatic metabolism studies, two aquatic dissipation studies, and two terrestrial dissipation studies.

Based on a review of all of the guideline laboratory and field studies conducted for malathion, the potential for malaoxon to form from malathion in the environment is concluded to be very small. It is for this reason, that EPA concluded on page 48 of its July 2006 Reregistration Eligibility Decision for Malathion that “the Agency does not expect malaoxon to be a significant component of the ecological hazard of malathion to non-target organisms”.

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